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THE ORDER OF CRYSTALLIZATION IN IGNEOUS ROCKS

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The order of crystallization in igneous rocks is necessarily determined from the end product, the solid rock. When thin sections of the holocrystalline rocks are examined the constituent minerals show certain relations of outline to each other that give some information as to the order of crystallization. The relations of outline referred to include: the idiomorphism of one mineral against another, the indentation of one mineral by another, and the complete inclosure of one mineral by another. It is one of the objects of this paper to inquire into the conclusions that may safely be drawn from observing these relations.

Fig. 1 is a diagrammatic section of a crystal of, say, plagioclase which incloses a few crystals of another mineral, say, magnetite. Only the outer rim *A* of this crystal can be safely assumed to be of later crystallization than the magnetite. The inner portion *B* may be of later crystallization but, on the other hand, may be earlier. The fact that magnetite is situated only in the peripheral portions would make one suspect the truth of the latter possibility, but from this selfsame crystal of plagioclase an endless number of sections could be cut in which there would be no evidence of this peripheral placing of the magnetite. Some sections would contain magnetite scattered throughout, even in the most central portions. *S* of Fig. 1 indicates the direction of such a section cut in a plane normal to, or at some high angle with, the

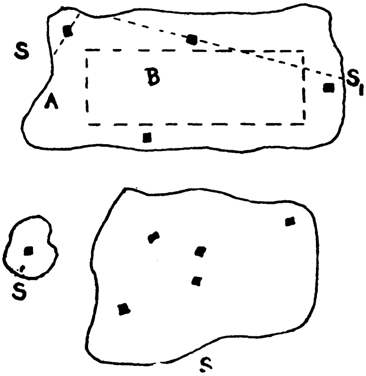

FIG. 1

plane of the page. S_1 indicates the direction of another section, cut as before, showing magnetite centrally placed in a plate of plagioclase, part of which is without doubt younger than the magnetite but part of which may be older. These sections are shown in plan in the figure. In the great variety of sections such as a rock slide commonly contains, some few would show a peripheral placing of the magnetites, but this would be regarded as mere accident in the face of the great number that showed a random placing. The conclusion as to order of crystallization would be that magnetite had crystallized before plagioclase, when as a matter of fact the greater proportion of the plagioclase might have crystallized before magnetite. Obviously the only safe conclusion that can be drawn is that *some* of the plagioclase continued to crystallize after magnetite had ceased to crystallize.

The conclusions that may be drawn from the fact that one mineral is idiomorphic against another or that one mineral indents another are qualified in a similar manner, as will be apparent from an examination of Figs. 2 and 3.

These figures represent sections of an augite crystal with a plagioclase crystal indenting it (Fig. 2) and idiomorphic against it (Fig. 3). The two cases are strictly analogous and do not require separate consideration. The relation of the minerals makes it apparent that only the outer rim *A* of the augite is necessarily of later crystallization than the plagioclase. The inner portion *B* may have crystallized later than, or simultaneous with, or earlier than, the plagioclase.

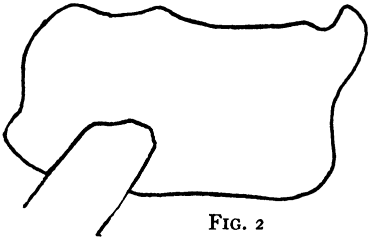

FIG. 2

The alternatives mentioned would, however, not be apparent in most other sections. *S* represents the direction of such a section, cut as before, and shown in plan in the figure. A natural conclusion from such sections (and a rock slide would show every variety) would be that augite crystallized after plagioclase when really the greater proportion of augite might have crystallized before. The relation of the two minerals indicates with certainty only that augite continued to crystallize after plagioclase had ceased. The order of cessation of crystallization is the only certain information given.

In Fig. 3 but one crystal is shown idiomorphic against the augite crystal. If a great many other crystals showed the same relation to the augite, in short, if the augite crystal were interstitial to a number of other minerals, no more definite conclusion than the above could be drawn. The augite crystal continued to grow after the others ceased, but it might have begun to form before the crystals to which it is interstitial.

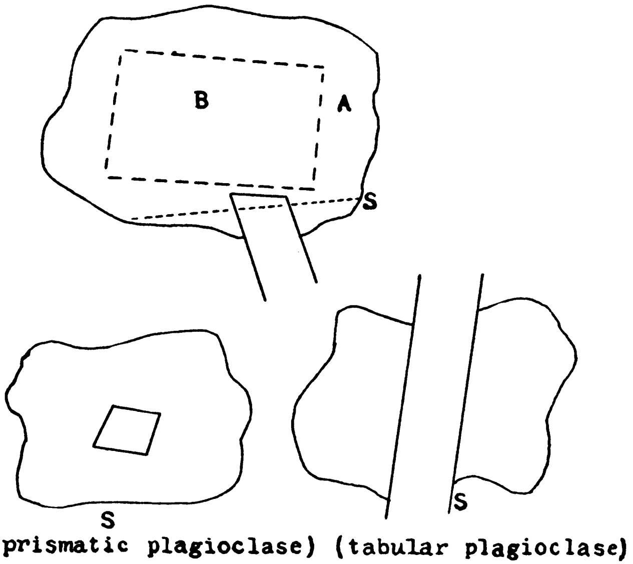

FIG. 3

Obviously, then, the observation of all[1] the relations of outline of a number of minerals in a section of a holocrystalline granular rock leads to a safe conclusion only as to the order in which the minerals have ceased to crystallize. Any statement of order of crystallization based on such observations should be modified to a statement merely of order of cessation of crystallization.

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[1] Cf. A. Harker, *The Natural History of Igneous Rocks*, 1909, p. 179.

THEORETICAL DISCUSSION

A theoretical discussion of the crystallization of rocks can, in the present state of knowledge, lead to but few definite conclusions. It is not at all clear why there should be in any rock an *order* of cessation of crystallization. If the final crystallization is that of a eutectic mixture there should be no such order. It may be pointed out, however, that the simple eutectic results only when each constituent lowers the melting-point of every other constituent. Solid solution often brings it about that there may be a raising, and with rocks, in which, as a rule, solid solutions (mix-crystals) are very common, it cannot be said what the combination of possible "raisings" and "lowerings" may result in.

Theory, then, helps very little in making any prediction as to what ought to happen. It can, however, be safely stated that in any system the tendency of special richness in a certain constituent will be in the direction of causing that constituent to *begin* to crystallize in the early stages. A "constant order of crystallization" capable of almost universal application to all rocks, whatever the variation in mineral proportions (Rosenbusch's rules), is from this point of view out of the question. The order stated is, however, based on considerations already discussed and is really only the order of cessation of crystallization. Why a certain order should be sufficiently common to be noticeable is not apparent, but it does seem more reasonable that this should be true of the order of cessation of crystallization for various rocks than of the order of beginning of crystallization.

ORDER OF BEGINNING OF CRYSTALLIZATION

If it is admitted that the "order of crystallization" as commonly stated for any rock is merely the order of cessation of crystallization, the question arises as to whether there is no clue to be had to the order of beginning of crystallization.

In laboratory practice[1] a method of following the course of crystallization in a mixture at high temperatures is to hold the mixture in a furnace at a definite temperature for a period of time and to quickly plunge the charge into a cool liquid which chills it instantly to a temperature at which further crystallization is permanently checked or rendered excessively rapid (metals). The examination of the chilled product reveals those constituents which had crystallized at the temperature of the furnace and by repeating at other temperatures the whole course of crystallization is followed. The method is known as the method of quenching.

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[1] J. H. L. Vogt, *Die Silikatschmelzlösungen*, I, 106; E. S. Shepherd and G. A. Rankin, *Am. Jour. Sci.*, XXVIII (1909), 293; C. H. Desch, *Metallography*, 1910, 210.

The "order of crystallization" commonly stated for granite is: accessories, ferromagnesian minerals, lime-alkali feldspar, alkali feldspar, quartz. This order is determined from the outline relations of the minerals of granites which, as we have seen, can give with certainty only the order of cessation of crystallization, but for the moment it will be assumed that the order is as stated and the consequences examined. The order may be represented diagrammatically as follows.[1]

If rocks of granitic composition could be found in which crystallization had proceeded to a certain stage and had then been checked, the product should show the following characteristics. Accessories in average amount comparable with that in granites should in general be present; the most common phenocrysts, very often the only phenocrysts, should be of the ferromagnesian minerals; in rocks in which crystallization had proceeded to a considerable extent lime-alkali feldspar should accompany the ferromagnesian minerals; with more complete crystallization alkali feldspar should accompany the preceding minerals, and in a rock largely crystalline quartz should appear in company with all the above minerals.

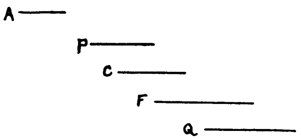

FIG. 4

In Figs. 4, 5, and 6, *A* indicates accessories, *P*, ferromagnesian minerals, *C* (calcialkalic) lime-alkali feldspar, *F*, alkali feldspar, and *Q*, quartz.

Thousands of rocks of granitic composition are known in which crystallization has been checked at various stages (rhyolites) but they show no such peculiarities as are to be expected from the above outline. They often show phenocrysts of quartz and alkali feldspar and of these alone with the greater part of the rock still glass. They may show phenocrysts of the ferromagnesian minerals and of lime-alkali feldspar but only in company with much alkali feldspar and quartz. Finally the accessories, instead of being almost universally present, commonly fail.

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[1] Cf. Pirsson, *Rocks and Rock Minerals*, 1909, 148.

The conclusion is that the order of beginning of crystallization in granitic magma is very different from the "order of crystallization" commonly stated, that is, from the order of cessation of crystallization. Regarding the rhyolites as quenched granites the order of beginning indicated is: (quartz, alkali-feldspar); (lime-alkali feldspar, ferromagnesian minerals); accessories. (Alkali feldspar may often begin before the quartz, and ferromagnesian minerals may often begin before lime-alkali feldspar, depending upon their amounts.) If the course of crystallization is represented in diagram the result will be somewhat as follows:

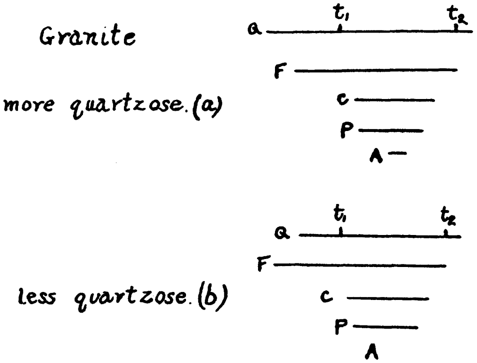

FIG. 5

The positions of the beginnings of the lines indicate the order of beginning of crystallization, and of the ends of the lines, order of cessation of crystallization. The vertical order of the lines themselves is chosen at random.

It may be objected that the crystals which a rhyolite shows often form while the rhyolite is on its way to the surface, or even after it has reached the surface, and are therefore formed under different conditions of pressure and perhaps in the presence of less mineralizers than in the case of the granite, with the result that the order of crystallization in granites is reversed in rhyolites. The likely effect of such changes of conditions is a slight displacement of equilibrium conditions, not the drastic change implied in the above statement, but apart from the question of likelihood there is the evidence of small deep-seated bodies to be considered. These bodies crystallize under conditions comparable with those for a granite except that the rate of cooling is greater. When of granitic composition these bodies persist in showing phenocrysts of alkali feldspar and often of quartz also (Fig. 5*a*).

A study of Fig. 5 shows how such a result is possible. Quartz and alkali feldspar begin to crystallize earliest and at first the viscosity is low (relatively) so that the crystals formed grow to a considerable size. At some temperature (t_1) viscosity has increased to such a value that crystallization of quartz and alkali feldspar must proceed in the quickly cooled body by the formation of new centers. The result is a rock with phenocrysts of quartz and alkali feldspar and a matrix showing a second "generation" of quartz and alkali feldspar together with the other minerals. In the case of the granite crystallization proceeds in a similar manner and at the temperature (t_1) viscosity has reached a comparable value but the progress of crystallization is much slower and continues to take place by addition[1] to the early quartz and alkali-feldspar crystals. Lime-alkali feldspar, ferromagnesian minerals, and accessories begin and cease to crystallize as the diagram indicates; quartz and alkali-feldspar crystals continue to increase in size. Feldspar ceases to grow at t_2. At this stage quartz, like the feldspar, locally shows idiomorphism against the small amount of remaining liquid, but in the further growth of the crystals their outline is determined by the space available. The result is that the quartz crystals have an interstitial relation and there is evidence of only one "generation" of quartz, although the interior parts of the crystals formed during the earliest stages of crystallization.

The diagram affords, therefore, a systematic explanation for the textural varieties of the granite-rhyolite group as a result of different rates of cooling. The commonly stated "order of crystallization" is contradictory to the evidence of these textural varieties.

The early beginning of crystallization of quartz and feldspar is in no respect contradictory to the relations seen in thin sections of granites. It accords with the fact that Lagorio[2] failed to find the universal progressive "acidification" of the residual base of volcanic rocks which the early crystallization of ferromagnesian minerals would necessitate. Finally it may be stated that from the theoretical side the early beginning of crystallization of quartz and alkali feldspar is to be expected in a rock whose chief characteristic is richness in quartz and alkali feldspar.

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[1] A. Harker, *op. cit.*, p. 267.

[2] *T.M.P.M.* (2), VIII (1887), 421–529.

It is possible, even probable, that Fig. 5 suggests too great a difference in time of cessation of crystallization of the various minerals. Certain it is that in most granites evidence of relative idiomorphism of the minerals does not leap to the eye. It must, as a rule, be carefully sought.

It may also be objected that the mode of formation of many rhyolites is of that nature which most favors supercooling with the possible result that the normal order of crystallization may suffer considerable change.[1] When, however, the quartz and feldspar phenocrysts of a rhyolite have attained considerable size they must have grown throughout a fair period of time in contact with fluid magma and therefore presumably in equilibrium with it. In short, they represent the normal early crystals.

Inductive reasoning leads one to the same conclusion. In at least some rhyolites crystallization was instituted in depth and proceeded slowly for some time before extravasation (quenching) according to the order for a granite since conditions were identical. Some quenched rocks of granitic composition should, then, show the characteristics already pointed out as consequent upon the commonly stated "order of crystallization" if this order really holds and if the observed early crystallization of quartz and feldspar is the result of supercooling or any such complication ensuant upon difference of conditions under which granites and *other* rhyolites crystallize. No quenched rocks of granitic composition which show these characteristics are, however, known to exist.

The resorption phenomena so commonly shown by the quartzes of a rhyolite might be taken as evidence that quartz may crystallize first in granitic magma, but is later resorbed and appears again only in the later stages. The gradation by insensible steps, often found in hypabyssal rocks, from vitrophyre through quartzporphyry and granite-porphyry to a normal granite, does not bear out this conclusion, and is explicable only on the basis of the order here deduced, and a gradual change in rate of cooling. Indeed, the resorption phenomena exhibited are best explained as due to the sudden change of conditions experienced by a rhyolite, especially the relief of pressure. The specific volume of quartz is 0.377 and of "quartz glass" 0.452 at 25°. The ratio of the values of these quantities at higher temperature is probably of the same order. The great difference between these figures indicates the strong tendency that the sudden relief of pressure would have in the direction of re-solution of quartz in a magma from which it had separated.

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[1] A. Harker, *op. cit.*, p. 213.

If the crystallization of other rocks as determined by taking the evidence of plutonic and effusive types regarded as their quenched equivalents is represented in diagram, we obtain,

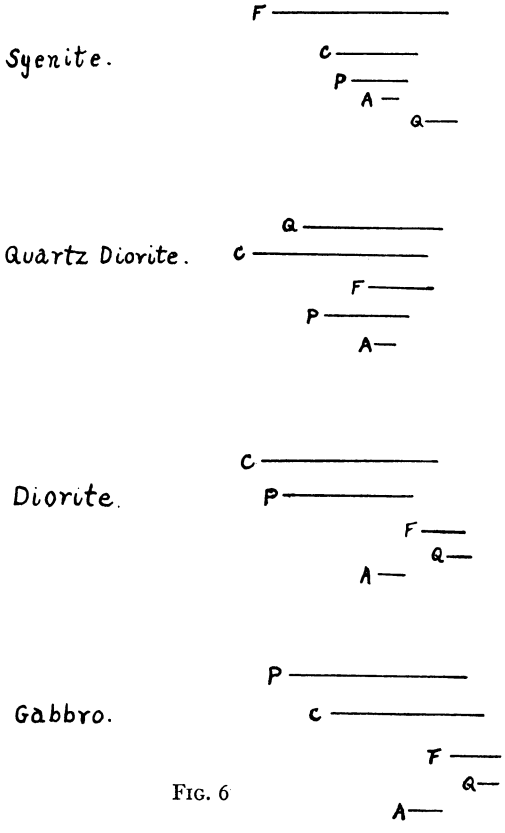

FIG. 6

For the systematic presentation of the deduced order of crystallization, the rocks (sub-alkaline) are treated in the broad types of systematic petrography. There is, of course, complete overlapping of the types and a similar gradual transition in order of beginning of crystallization. For example, the granite by increase of lime-alkali feldspar relative to alkali feldspar passes to the quartz diorite, and in the quenched equivalents alkali feldspar becomes less and less important as a mineral of early consolidation and lime-alkali feldspar more important, the result being a like passage from rhyolite to dacite. Again, the granite passes into the syenite by gradual decrease in quartz, and in the quenched equivalents quartz is represented in less and less amount as a mineral of early consolidation giving the passage from rhyolite to trachyte.

In short, there is abundant evidence throughout of the tendency of special richness in any constituent to cause the early beginning of crystallization of that constituent as theory would lead one to expect. In every case a plutonic type whose distinguishing characteristic is richness in a certain mineral, or pair of minerals, has for its equivalent effusive type a rock whose chief characteristic is the appearance of this constituent or pair of constituents as minerals of early consolidation.

It is hard to conceive a reconciliation of these well-known facts with the statement of any approximately constant "order of crystallization" on the basis of which accessories, ferromagnesian minerals, and lime-alkali feldspar should always be the minerals of early crystallization.

The broad generalization which is necessary when any type is represented by a single diagram is perhaps likely to lead to some misunderstanding. In the gabbro diagram, for example, the ferromagnesian minerals are represented as beginning first, but this must be regarded as true only for the more femic gabbros. In a gabbro approaching anorthosite, plagioclase undoubtedly begins to crystallize considerably before the ferromagnesian minerals. The difficulty is inherent in the breadth of the types.

The chief desire has not been to establish definitely the course of crystallization for all rocks referable to a given type, but to indicate it for the average rock of any type in order that emphasis may be placed upon the importance of the effusive types as evidence of the order of beginning of crystallization and upon the distinction between order of beginning of crystallization and commonly stated "order of crystallization" (order of cessation of crystallization).

CONSEQUENCE UPON THEORIES OF DIFFERENTIATION

Variation in composition in different parts of a single rock body, or in closely associated separate bodies, is usually discussed in terms of order of crystallization of the constituent minerals. In nearly all cases the constant order of crystallization of Rosenbusch is assumed, whatever the composition of the magma treated. For example, the more femic upper portions of a granitic batholith that are so often observed have been explained as due to the early crystallization of ferromagnesian minerals at the cool contact and the continued diffusion in that direction of femic material, the result being an enrichment near the contact in ferromagnesian minerals. Apart from the question as to whether diffusion could take place and whether it would be better to appeal to convection as the mechanism of transfer, there is the fundamental question of the truth of the assumption that the ferromagnesian minerals crystallize early in granites. If it is recognized that quartz and feldspar are the minerals of early crystallization in granitic magma, the explanation is out of the question. Possibly early crystals of quartz and feldspar settled out of the contact portion.

A discussion of differentiation is not, however, intended here, and the above suggestion is made merely to show the extent to which views on differentiation may be altered by a recognition of the distinction between order of beginning of crystallization and order of cessation of crystallization (commonly stated "order of crystallization").

SUMMARY

1. The criteria for the determination of "order of crystallization" of rock minerals as applied in thin sections are discussed and it is shown that only order of cessation of crystallization can be so determined.

2. The order of beginning of crystallization is shown in the effusive types, which may be regarded as the "quenched" equivalents of plutonic types.

3. Taking the evidence of both the plutonic and effusive types, diagrams are given indicating the course of crystallization in granite, syenite, quartz diorite, diorite, and gabbro.

4. Certain consequences upon theories of differentiation are pointed out.

The writer is indebted to Professor J. P. Iddings for helpful suggestions.